

PATENT SPECIFICATION

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C2C8 C2C9 C2CX

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(54) AMPHOTERIC POLYMERS AND PROCESS FOR THEIR USE

(71) We, I.W.S. NOMINEE COMPANY LIMITED, a British Company of Wool House, Carlton Gardens, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

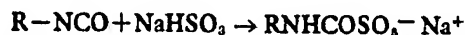
This invention relates to polymers capable of further reaction and more especially relates to such compounds having both anionic and cationic groups in the molecule. It also relates to methods of treating keratinous fibres to confer shrink-resistance.

Wool fabrics can be made shrink-resistant, either before or after dyeing, by means of a chemical oxidative treatment, e.g. chlorination. However, with all degradative treatments a high level of washability can only be obtained at the cost of weakening the wool fibre.

High resistance to felting shrinkage without a deterioration of physical properties can be achieved by the application of a prepolymer from aqueous solution, but there remains a need for a shrink-resist resin that can be exhausted on to wool fabric or garments from a long liquor, without the need for pre-chlorination.

Isocyanate-terminated resins are commercially available for application to wool piece goods from chlorinated hydrocarbon solvents. Methods have been described by which these products can be emulsified and exhausted on to wool piece goods from long liquors as in British Patent No. 1,262,977. However, the emulsions are unstable owing to reaction of the isocyanate groups with water.

The free isocyanate groups of an isocyanate-terminated polyether type urethane prepolymer can be reacted with sodium bisulphite according to British Patent No. 1,419,306 to yield an anionic product which contains bisulphite blocked isocyanate groups — as in equation (1):



(1)

This water-soluble compound is an effective shrink-resist agent for wool piece goods when applied by a pad-dry technique. Being anionic in character it behaves in the same way as an anionic wool dyestuff and exhausts on to the fibre from long liquors under slightly acid conditions. However, unlike a dyestuff, the prepolymer, because of its large molecular size, does not diffuse into the fibre but is confined to the surface. For the resin to confer shrink-resistance it should be cross-linked, which is best done under alkaline conditions. As soon as the pH of the exhausted liquor is increased then the anionic resin is desorbed from the surface of the wool faster than the blocked isocyanate groups can yield urea cross-links. Polymerisation may then take place in the bath leading to precipitation on to the fabric and thus to a sticky handle.

The compounds of the present invention are cross-linkable polymers containing cationic groups whereby they have affinity with wool fibres as well as anionic groups. The preferred compounds provide stable, water dispersible, amphoteric prepolymers which can be exhausted on to unchlorinated wool fabric together with dyestuffs, have

dye levelling properties and can be cured, after exhaustion, to produce a shrink-resist finish.

The amphoteric polymeric compounds of this invention comprise at least one polymeric chain and both anionic and cationic groups, and contain per molecule at least two reactive groups capable of cross-linking either directly or by means of a cross-linking agent. The cross-linkable groups may be constituted by the anionic or cationic groups or may be distinct and possibly un-ionized groups.

The invention further provides a method of making curable polymeric compounds for the treatment of keratinous fibres in which prepolymers, which may already contain some of the necessary groups, are reacted to introduce anionic and/or cationic and/or cross-linkable groups to result in a polymeric compound containing the groups required for the purposes of this invention, either by introduction or partly by retention.

The invention also provides a process of treating keratinous fibres by applying a curable compound of this invention by exhaustion from an aqueous bath and curing the compound on the fibres. Keratinous fibres treated by this process and therefore bearing the cured product of a compound of this invention are also included within the scope of the invention.

The preferred polymeric chains in the compounds of this invention are polyether, polyester, polyamide or polyurethane chains, but polyether chains are especially preferred. They may readily be produced by condensation of alkylene oxides, and a variety of prepolymers containing such chains, and terminated by hydroxyl groups or by reactive groups such as thiol or isocyanate, are commercially available and may be used as starting materials in the preparation of the curable compounds of this invention.

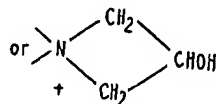
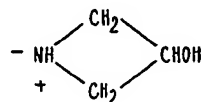
The cationic groups in the compounds of this invention may comprise for example, protonated amino groups, azetidinium, pyridinium, isothiuronium and sulphonium groups. Phosphonium groups may be effective but are difficult and expensive to obtain. Some of these groups may themselves take part in cross-linking reactions.

These groups may be linked in or to the polymeric chains in a variety of ways, among which are the following:

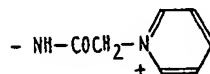
protonated amino groups



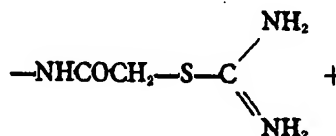
azetidinium groups



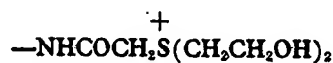
pyridinium groups



isothiuronium groups



sulphonium groups



The anionic groups which are also present may be thiosulphate groups $-\text{SSO}_3^-$ (Bunte salts) or carbamoyl-sulphonate groups $-\text{NHCOSO}_3^-$ (bisulphite adducts)

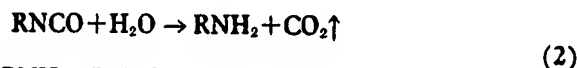
of isocyanates). Both these groups are themselves reactive and cross-linkable under appropriate conditions, but other anionic groups, such as carboxylic and sulphonic acid groups, can be used provided there are other and cross-linkable groups present in the molecule.

5 It may be noticed that in many cases the anionic or cationic groups are substituent groups but this is not necessarily so, and the charged groups may constitute part of the polymeric chain or backbone, as for example in the case of protonated nitrogen atoms.

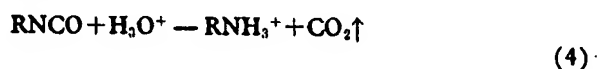
10 Uncharged cross-linkable groups may be present and, where only non-reactive cationic and anionic groups are present, may afford all the cross-linking capacity required to form a curable polymer. Examples of such cross-linkable groups include isocyanate and thiol groups (the latter being slightly ionized in alkaline conditions).

15 The compounds of the invention may be made by treating a solution in an organic solvent of a compound containing at least one polyether, polyester, polyamide or polyurethane chain and at least two isocyanate groups with a strong mineral acid.

The reactions by which isocyanates produce cross-links in the presence of water are shown by equations (2) and (3):



20 We have found that isocyanate terminated prepolymers react with concentrated mineral acids, when in solution in an organic liquid, in the presence of water, to produce protonated amino groups, as in equation (4):



25 The amount of water present during this reaction must, of course, be sufficient for formation of the hydroxonium ion.

30 The protonated amino groups are unreacted towards isocyanate groups and a reaction similar to (3) does not occur. The number of charged amino groups produced has been found to be directly related to the amount of mineral acid used, one mole of sulphuric acid hydrolysing two moles of isocyanate, including conversion of all of the isocyanate groups.

35 According to a further aspect of the present invention there is provided a polymeric compound which comprises at least one polyether (especially polyoxyalkylene), polyester, polyamide or polyurethane chain, p cationic groups and q anionic groups per molecule, wherein $p+q$ is at least 2 and the molecule contains r cross-linkable groups, wherein r and $p+q+r$ are both at least two. Where the cationic groups are reactive in cross-linking $r \geq p$. Similarly, where the anionic groups are reactive, $r \geq q$. The average value for p (or q) may have any value above zero, but the values of p and q for any individual molecule will be integral. Preferably, $p+q=3$, and it is especially preferred that p be 1 and q be 2.

40 Such a compound will exhaust on to wool over a wide pH range and can be cured on the wool under alkaline conditions. The invention includes such a process of treating keratinous fibres, and fibres so treated.

45 Examples of cross-linkable groups which may be used in the preferred compounds include isocyanate bisulphite adducts $\text{—NHCOSO}_3\text{—}$ and Bunte salts $\text{—SSO}_3\text{—}$. The latter may be introduced by reacting the precursor with chloroacetic acid and treating with sodium thiosulphate to replace the Cl with $\text{—SSO}_3\text{—}$.

Compounds containing the former type of group can be prepared by a two-stage method:

- 50 (a) partially hydrolysing the isocyanate groups of a poly-isocyanate prepolymer with a mineral acid (as equation 4);
- (b) reacting the remaining isocyanate groups with sodium bisulphite to form the bisulphite adduct (as equation 1).

55 For stage (b) it is important to maintain a homogeneous solution of resin and sodium bisulphite by adjusting the proportions of water and water miscible organic solvent, as described in Belgian Patent No. 795,575.

The final product is amphoteric because it contains both amino groups, which are cationic under neutral to acid conditions, and bisulphite blocked isocyanate groups, which are anionic. Experiments have shown that compounds of this type, prepared

from polyisocyanate shrink-resist resins, exhaust readily on to keratin fibres over a wide range of pH values.

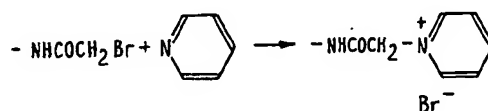
If exhaustion is carried out below pH 6 then cross-linking in the bath does not occur since the bisulphite blocked isocyanate groups are stable under acid conditions. Cross-linking of the absorbed resin can be brought about by increasing the pH of the bath. Desorption of the resin does not occur under the alkaline conditions required for cross-linking. A further advantage is that if a dyestuff is exhausted on to the wool at the same time as the resin, then the latter acts in a similar manner to conventional amphoteric dyeing auxiliaries and promotes level, non-skittery dyeings.

The ratio of cationic to anionic groups can be varied at will simply by altering the amount of acid used to promote the reaction shown in equation (4). It is assumed that all the free isocyanate groups remaining after this stage react according to equation (1). There is in fact an optimum ratio of cationic to anionic groups which produces both good exhaustion and excellent shrink-resistance and this is found to be about 60:40. However, if the ratio of protonated amino groups is increased, optimum cross-linking may be restored by adding formaldehyde, or a formaldehyde source, to the bath.

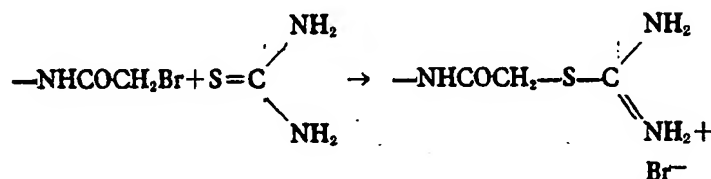
Polyisocyanate-terminated prepolymers can also be used as the starting point for polymeric compounds with other cationic or anionic groups.

For example, some or all of the terminal isocyanate groups may be reacted with a halocarboxylic acid, such as bromoacetic acid. The resulting bromide can be reacted with a variety of reagents as follows:

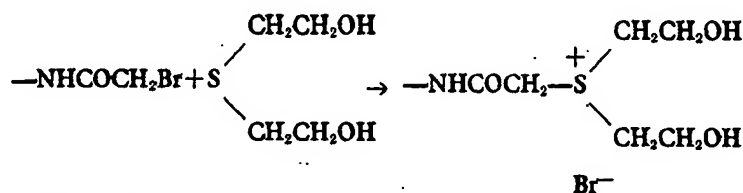
with pyridine to form a pyridinium group



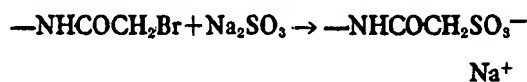
with thiourea to form an isothiuronium group



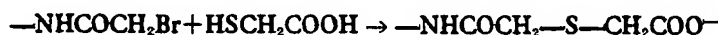
with thiodiglycol to form a sulphonium group



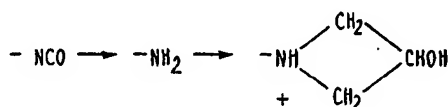
with sodium sulphite to form a sulphonate group



with thioglycolic acid to form a carboxyl group



Alternatively, terminal isocyanate groups can be partly or completely hydrolysed to amino groups and the amino groups reacted with epichlorohydrin and alkali to form azetidinium groups:



Partial reaction with one reagent can give partial substitution of the available centres with a particular cationic or anionic group and subsequent reaction with another reagent can give partial or complete substitution of the remaining centres with a different group, respectively anionic or cationic. The selection of appropriate reaction conditions and stoichiometric quantities are well within the normal skill of the expert, having regard also to the Examples given hereinafter.

Another type of cross-linkable group that can be employed in compounds of this invention is the thiol group. Since thiol groups are slightly ionised in alkaline solution they can confer a slight amphoteric character on a compound in which they occur along with cationic groups. Moreover, thiol groups in an existing prepolymer can be used in reactions to introduce other groups, cationic or anionic, and residual thiol groups can provide the necessary cross-linking capacity.

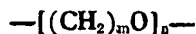
For example, a diisocyanate can be partly hydrolysed with mineral acid to form a protonated amino group and the remaining isocyanate group reacted with a thiol group on the prepolymer to link the cationic amino group to the prepolymer.

It has been found that the effectiveness of amphoteric compounds according to this invention in preventing shrinkage of wool textiles in washing varies with the ratio of cationic:anionic groups in the polymer. It is preferred that this ratio should lie in the range from 45:55 to 65:35, the most preferred ratio being about 60:40. Below 40% of cationic groups exhaustion is substantially reduced while above 70% cationic groups the polymer does not spread as readily on unchlorinated wool to form the film necessary for effective shrink-resistance.

In the accompanying drawing the single Figure is a plot of area shrinkage, after a 3-hour wash, against the cationic:anionic ratio (expressed as % cationic groups) for a trifunctional isocyanate prepared from a 3000 m.w. polyether triol and hexamethylene diisocyanate in which the cationic groups are supplied by acid hydrolysis of isocyanate to protonated amino groups. It appears, however, that the variation of effectiveness with cationic:anionic ratio is essentially similar with all amphoteric polymers having cross-linking capacity, and satisfactory results have been obtained with a wide variety of combinations of groups at the preferred ratio, as will be shown hereinafter.

Examples of polyether chains which may appear in compounds of the invention include: polyoxyethylene, polyoxypropylene and, because of their excellent light stability, especially polytetramethylene oxide chains. The term 'polyether' is also intended to include polythioethers, such as condensations of thiodiglycol. Examples of polyester chains include polyester chains produced by reacting dicarboxylic acids, such as adipic acid, malic acid, terephthalic acid, sebacic acid, malonic acid and itaconic acid, with diols such as hexanediol, ethylene glycol or diols of the type $HO-(C_mH_{2m}O)_n-H$ where m is 1 to 12 and n is 1 to 50.

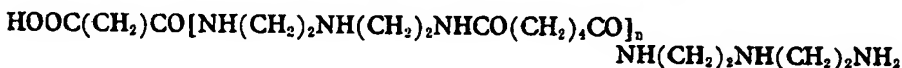
We have found that with cross-linkable compounds based on polyether (polyoxy-alkylene) chains, the light fastness of shrink-resist finishes on keratin fibres is greatly enhanced when the alkylene groups in the polyether chains have unbranched carbon chains of three, or preferably four or more carbon atoms, i.e. when the poly(oxy-alkylene) chains have the formula



wherein m is at least 3 and preferably 4, and n is at least 1, provided that where n is 1, m is at least 10.

Although the invention does not depend for its utility on any particular theory, it is believed that the presence of chains in the alkylene groups, as are present in the usual oxyalkylene polymers prepared from propylene or butylene oxide, lead to more ready breakdown of the chains on exposure to light, as occurs also with the very short ethylene chain.

Polyamide chains which may be present include, for example, polyhexamethylene adipamide and polycaprolactam chains, and also chains of the type:



Polyurethane chains which may be employed include, for example, those formed by the reaction of diisocyanates such as hexamethylene diisocyanate (HMDI) or toluene diisocyanate (TDI) with a diol such as those listed above.

Suitable isocyanate prepolymers to use in the preparation of amphoteric resins are those containing at least two isocyanate groups per molecule and preferably with a molecular weight of at least 500. These may be:—

(1) The result of co-reacting simple isocyanates with, for example, water, themselves or other isocyanates, e.g. Desmodur N (Bayer) which is formed by the reaction of 3 moles of hexamethylene diisocyanate and 1 mole of water.

(2) Prepolymers formed by the reaction of a compound containing more than one active hydrogen atom with an appropriate number of moles of the diisocyanate.

Suitable compounds include polyols, polyamines, polyamides, polycarboxylic acids, polythiols, hydroxy or carboxyl terminated polybutadienes, hydroxy or amino terminated silicones. These compounds may also be:

(a) polyethers, e.g. obtained from the polymerisation of ethylene oxide, propylene oxide, tetrahydrofuran, butylene oxide, or their copolymerisation or graft polymerisation products; or obtained by condensation or alkoxylation of polyhydric alcohols;

(b) polythioethers, e.g. from the condensation of thiodiglycol with itself and/or with other glycols, dicarboxylic acids, formaldehydes, amino carboxylic acids or amino alcohols;

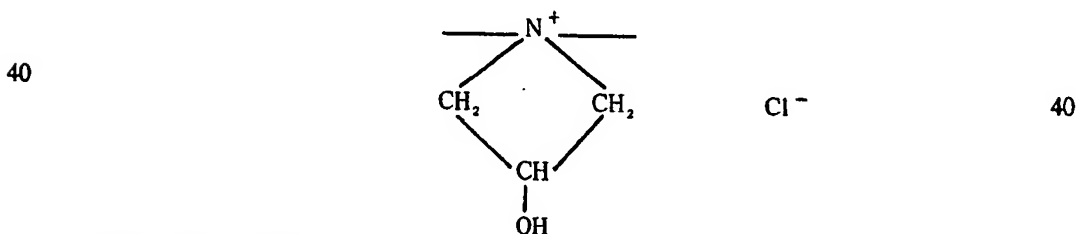
(c) polyesters, e.g. derived from polybasic, saturated or unsaturated carboxylic acids (or anhydrides) and polyvalent, saturated or unsaturated alcohols, amino-alcohols, diamines, polyamines or mixtures of these; or polyesters of lactones, such as caprolactone;

(d) polycarbonates;

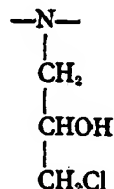
(e) natural oils, such as castor oil.

Examples of polyisocyanates suitable for reaction with the above compounds are as follows: aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, cyclo-aliphatic diisocyanates such as cyclohexane-1,4 - diisocyanate, 4,4' - dicyclohexylmethane diisocyanate and 2,4 and 2,6 - hexahydrotolylene diisocyanate, araliphatic diisocyanates such as *p* - xylylene diisocyanate, aromatic diisocyanates such as *p* - phenylene diisocyanate, 1 - chloromethylphenyl-1,4 - diisocyanate, 1 - bromomethylphenyl - 2,6 - diisocyanate, dimer acid diisocyanates, 2,4- or 2,6-tolylene diisocyanate.

A preferred compound of the invention having a polyamide chain and $-\text{SSO}_3^-$ anionic groups may be prepared, for example, from a commercially available shrink-resist resin (Hercosett 57) which comprises a polyamide chain and pendant azetidinium ions:



and/or *N*-chlorohydrin groups:

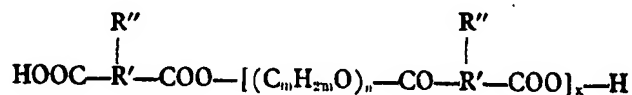


This resin may be treated with a solution of a water-soluble thiosulphate to replace some or all of the Cl groups with $-\text{SSO}_3^-$ ionic groups, thus giving a resin with protonated (tertiary) amino groups and anionic Bunte salt groups.

Another and particularly preferred type of compound according to this invention can be prepared from prepolymers comprising one or more polyether chains linked

and/or terminated by dicarboxylic acid residues, at least two of which residues contain cross-linkable substituent groups.

Such prepolymers can be prepared by reaction between polyether diols and functionally substituted dicarboxylic acids, the molar ratio between the diol and the acid governing the number of functional groups per molecule, and are described in Specification No. 1 480 213. They may be reacted to introduce cationic or anionic groups, for example into the dicarboxylic acid residues, as represented by the general formula:



where R' is a trivalent organic residue, R'' is or contains a cross-linkable or cationic group, x is at least 2, n is at least 1 and (C_mH_{2m}O) is a straight chain oxyalkylene group wherein m is at least 3 and where n is 1, m is at least 10, provided that the molecule contains at least one cationic R'' and at least two cross-linkable R'' (which need not be mutually exclusive).

One particular compound is prepared by reacting 4 moles of a thiol acid such as thiomalic acid with 3 moles of a poly(tetramethylene oxide) and subsequently reacting at least one thiol group per molecule with a compound including a cationic group, such as a diisocyanate in which one isocyanate group has been hydrolysed to an amino group.

The preferred compounds of the invention form particularly effective shrink-resist resins for keratinous fibres. Keratinous fibres which may be treated include cashmere, vicuna, mohair, hair, llama and especially wool. The fibres may be treated as loose stock, tops, slubbings, yarns or fabrics, woven, non-woven or knitted.

A further advantage of these resins lies in their ability to impart a smooth drying finish to fabrics. Thus, it is possible to produce permanent press fabrics by an exhaust rather than a padding technique.

The treatment may be carried out in conventional textile machinery and it is an advantage of the compounds of the invention that they will exhaust on to wool from long liquor baths without the necessity for oxidative pretreatment of the wool, such as chlorination. Furthermore, the preferred compounds which are applied under acid conditions can be applied in the dye bath either before, after or simultaneously with dyeing, when they have the advantage that they promote level dyeing. In the latter case it may not be necessary to use a conventional dye levelling agent.

All classes of anionic dyes normally used for the coloration of wool may be used: e.g. acid levelling, acid milling, 1:1 premetallised, 1:2 premetallised, chrome and reactive dyes.

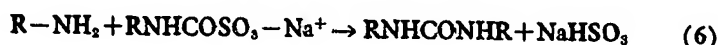
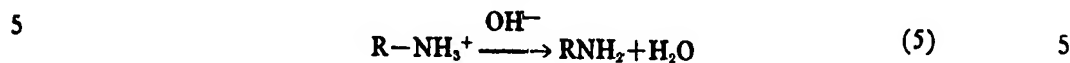
In applying the compounds to wool the pH of the treatment bath may vary widely, more especially from pH 2 to 11. In the case of the majority of amphoteric polymers, however, it is preferred to use a liquor pH of 2 to 6, since the polymers are most stable under slightly acid conditions. Inorganic salts, such as sodium sulphate, sodium chloride and ammonium sulphate, assist exhaustion. Selected wetting agents such as Aerosol OT (Cyanamid), Lissapol N (ICI) and Silicone L77 (Union Carbide) have been found useful in assisting level exhaustion.

Some polymers, however, such as those having thiol groups as the cross-linkable groups, may be applied in weakly alkaline solution, for example at pH 7-9.

A wide range of temperatures of application can be used. With some compounds room temperature may be suitable but with most compounds it is preferred to exhaust at elevated temperatures up to and including the boil. In one often preferred procedure the temperature of the bath is increased slowly from 25°C. Exhaustion is usually complete by the time the temperature reaches 70°C to 80°C, but heating may be continued until boiling.

Once exhausted on to the wool, the prepolymer may be cross-linked to complete the formation of the resin product. Curing can be brought about by dry heat or by raising the pH of the bath to a value above pH 7.5, since the great majority of cross-linkable cationic or anionic groups employed herein are curable under alkaline conditions in an alkaline bath occurs at any temperature above ambient, the rate increasing with temperature. Particularly useful conditions are 10 minutes at 70°C and pH 8.5, since this is often used for the after-treatment of some classes of reactive dye. Curing by dry heat, which may be used for example with thiol groups, can be combined with drying of the treated fibres after removal from the exhaustion bath.

Although the usefulness of the invention in no way depends on any theory or mode of operation, we believe that, in the case of compounds with amino and bisulphite adduct groups, de-protonation of the amino groups occurs, followed by reaction with the bisulphite blocked isocyanates, according to equations (5) and (6):



Under alkaline conditions the bisulphite adduct of the isocyanate may simply unblock (reverse of equation (1)) and then react according to equations (2) and (3). In both cases the product is a substituted urea.

10 Curing of other cross-linkable groups or combinations of groups takes place by the mechanisms usually associated with such groups, as for example in the curing of thiol compounds with the formation of disulphide linkages. 10

The invention will be further illustrated by the following Examples. In the Examples commercial grade reagents are used thereby producing the water necessary for production of hydroxanium ions, where necessary. 15 15

Example I.

A trifunctional isocyanate prepared from a 3000 molecular weight polyether triol and HMDI (Synthapret LKF) (125 g of the 80% solution in ethyl acetate, as supplied by Bayer) was diluted with ethyl acetate (20 g). The solution was stirred while sulphuric acid (3 g) mixed with ethyl acetate (10 g) was added slowly. Stirring was continued for a further thirty minutes after the last addition. To this mixture was added isopropanol (160 g) followed by a solution of sodium metabisulphite (10 g) in water (60 g). Stirring was continued until the infrared spectrum showed the disappearance of the characteristic isocyanate peak at 2280 cm^{-1} (usually overnight). The product was a water clear solution with a solids content of 35% and a molar ratio of cationic to anionic groups, as determined by filtration, of 60:40. 20 25

The product from the above preparation (1.4 g of 35% solution) was mixed with a wetting agent (Aerosol OT75, Union Carbide) (0.16 g) and then diluted to 300 ml. with water at 25°C . Acetic acid was added to pH 4—5. A previously wet-out sample of an all-wool fabric (see Table I) (10 g) was immersed in the liquor, followed by a solution of anhydrous sodium sulphate (2 g) in water. The temperature was raised at the rate of $2\text{--}4^\circ\text{C}/\text{minute}$ to the boil, with occasional stirring. The liquor cleared progressively as the resin exhausted on to the fabric. Boiling was continued for 5 minutes, after which the liquor was cooled to 70 to 80°C . The pH of the bath was adjusted to a value of pH 8—9 and the temperature maintained at 70 to 80°C for 15 minutes. The fabric was hydroextracted, dried for 20 minutes at 100°C and then semi-decated for 3 minutes steam and 1 minute vacuum. The handle was excellent. Table I shows the anti-felt effect obtained by this procedure on various fabrics, the fabrics being tested by washing in a 15-litre Cubex machine. 30 35

TABLE I

Fabric	% Area Shrinkage After 3 Hours Wash	
	Untreated	5% Resin
Serge	64	2
Doctor flannel (unbleached)	62	0
Single jersey fabric (2/28's yarn to a cover factor of 1.1)	70	3
Single jersey fabric (Shetland)	65	2

Example II.

The product from Example I (1.7 g) was mixed with Aerosol OT75 (0.2 g) and diluted with water to 300 ml. To this was added predissolved sodium sulphate (2 g) and acetic acid to pH 4—5. The fabric (see Table II) was wet-out in this liquor for 10 minutes at 35°C and then a solution of wool dyestuff (eight reactive dyes, a pair of 1:1 premetallised and one 1:2 premetallised dye as identified in Table II) was added with stirring, while the temperature was slowly increased at 2°C/minute to 70°C, where it was held for 15 minutes. The temperature was then increased slowly to the boil, where it was held for 20 minutes. After cooling to 70—80°C the pH of the bath was adjusted to 8.5—9 by the addition of sodium carbonate. After a further 15 minutes the sample was hydro-extracted, dried for 20 minutes at 100°C and semi-decated for 3 minutes steam and 1 minute vacuum.

The handle of the fabric was excellent and the dyeing level and non-skittery compared with similar dyeings carried out in the absence of any levelling agent. The felting resistance was tested by washing tests similar to that of Example I.

TABLE II

Dyestuff	Fabric	% Area Shrinkage	
		1 Hour	3 Hours
Drimalan Brilliant Blue F2RL (Sandoz)	Serge	0	1
—ditto—	Unbleached doctor flannel	2	2
—ditto—	Single jersey	1	3
Drimalan Red F2GL (Sandoz)	Unbleached doctor flannel	1	2
Drimalan Blue F2GL (Sandoz)	—ditto—	2	2
Lanasol Red 6G (C.I. Reactive Red 84)	—ditto—	3	2
Lanasol Blue 3G (C.I. Reactive Blue 69)	—ditto—	3	3
Procion Turquoise Blue HA (C.I. Reactive Blue 71)	Serge	0	-2
Neolan Flavine GFE (C.I. Acid Yellow 103) (2 parts) Neolan Navy-blue 2RLC (Ciba-Geigy) (1 part)	Serge	0	0
Irgalan Grey BL (Ciba-Geigy)	Serge	1	0

Example III.

An isocyanate terminated prepolymer was prepared by reacting a 3000 molecular weight triol (Polyurax G300; B.P. Chemicals) (300 g) with an 80:20 mixture of 2:4 and 2:6 toluylene diisocyanate (Suprasec EN, I.C.I.) (46 g) until the free isocyanate content of the mixture had decreased by 50%.

To a solution of this product (25 g solids) in ethyl acetate (100 g) was added "Synthappret LKF" (62.5 g of the 80% product are supplied). The mixture was refluxed for 45 minutes. After cooling to room temperature, a solution of concentrated sulphuric acid (1 g) in ethyl acetate (10 g) was added over a period of 10 minutes with stirring, which was continued for 30 minutes after the last addition. Isopropanol (200 g) was added, followed by a solution of sodium metabisulphite (6 g) in water (20 g). This homogeneous mixture was stirred overnight to yield a clear solution with a resin solids content of 21%.

The product (4% resin solids on the weight of fabric — o.w.f.) was applied to wool serge, together with 1% o.w.f. Drimalan Brilliant Blue 2RL as described in Example II. The fabric was evenly dyed and had an area felting shrinkage, after being washed for 3 hours, of only 3% compared with 64% for an untreated sample.

Example IV.

In a combined dye-resin exhaust treatment the resin is usually fully exhausted before the dyestuff. The prepolymer may, if preferred, be cured at any stage after exhaustion, and not necessarily at the end of the processing sequence.

In an example illustrating this, the product from Example I (1.4 g) was mixed with Aerosol OT75 (0.16 g) and then diluted to 300 ml with water at 25°C. Acetic acid was added to pH 4. A previously wet-out sample of an all-wool single jersey fabric (10 g) was immersed in the liquor, followed by a solution of anhydrous sodium sulphate (2 g) in water. Xylene Fast Blue P (C.I. Acid Blue 82) (0.1 g) pre-dissolved in water, was then added and the temperature increased at the rate of 2—4°C/minute, with continuous stirring, to 80°C where it was held for 20 minutes. After this time the resin had exhausted. The bath was adjusted to pH 8.5—9 by the addition of ammonium hydroxide and stirring continued for 15 minutes. Formic acid was then added to bring the pH to 3 and heating continued to the boil. After 20 minutes at the boil the fabric was rinsed, dried, and semi-decated.

The fabric was evenly dyed and had an area felting shrinkage of only 5% after 3 hours washing, compared with that of an untreated sample of 65%.

Example V.

A difunctional isocyanate prepolymer based on a polybutylene oxide diol (Adiprene LS, Dupont) (120 g) was dissolved in ethyl acetate (100 g) and a solution of concentrated sulphuric acid (9.8 g) in ethyl acetate (25 g) was added slowly and carefully with stirring. After the last addition stirring was continued for a further 30 minutes. The product was diluted with isopropanol and a solution of sodium metabisulphite (12 g) in water (50 g) was added. Stirring was continued until the I.R. spectrum showed the disappearance of the isocyanate peak at 2280 cm⁻¹. Water or isopropanol were added as required to maintain a homogeneous solution throughout the reaction. The final product had a resin solids content of 20%.

A sample of this product (5% resin solids o.w.f.) was exhausted on to wool serge, together with 1% o.w.f. Drimalan Brilliant Blue 2RL, as described in Example I. The treated fabric showed zero area felting shrinkage after being washed for 1 hour as in Example I.

Example VI.

Trimethylol propane (13.4 g) was reacted with Adiprene LS 570 (360 g) by heating, with stirring, at 150°C for 5 hours. After this time reaction was judged to be complete since the free isocyanate content had decreased by 50%. This product (20 g) was dissolved in ethyl acetate (50 g) and a solution of concentrated sulphuric acid (0.45 g) in ethyl acetate (5 g) was added slowly with stirring, which was continued for 45 minutes after the last addition. Isopropanol (100 g) was then added followed by a solution of sodium metabisulphite (4 g) in water (20 g). More water was added until a clear solution was obtained. Stirring was continued overnight. The product had a resin solids content of 15%.

A sample of the above material (5% o.w.f.) was exhausted on to wool serge together with Drimalan Brilliant Blue 2RL (1% o.w.f.) as described in Example I.

Example VII.

This was carried out as in Example II except that as wetting agent 1% o.w.f. Silicone L77 (Union Carbide) was used instead of Aerosol OT.

The dyeing was level and non-skittery and the fabric shrank by only 2% after 3 hours' washing, compared with a shrinkage of 64% for an untreated sample.

Example VIII.

A sample (0.1 g resin solids) of the product from Example I was mixed with 0.03 g Aerosol OT and then diluted to 400 ml with water at 40°C. Woollen doctor flannel (10 g) was wet-out in this solution and stirred for 5 minutes. A prediluted dispersion (1 g) of a 50% acrylate polymer (Rohm & Haas N485) was added slowly with stirring. The pH was adjusted to 4 and the bath heated slowly to 80°C, by which time exhaustion was complete. The sample was then after-treated at pH 9 and 70°C for 10 minutes, followed by drying for 10 minutes at 120°C and steam-pressing for 3 minutes.

When washed for 1 hour the sample shrank by 3% area, compared with 64% for an untreated sample of the same fabric.

In the following Examples IX—XX the polymers employed were prepared from Synthapret LKF (Bayer). This compound is the reaction product of a polyether triol and hexamethylene diisocyanate. (Mol. Wt. 3000—3500). However, similar compounds can be prepared from products with other backbones capped with other isocyanates (both aromatic and aliphatic). In all these examples the ratio of cationic to anionic groups is about 60:40.

Example IX.

(Sulphonium and carboxyl groups)

Synthapret LKF (11.5 g of solids) was reacted with bromoacetic acid (1.42 g) until all the isocyanate groups had reacted. The product was dissolved in a mixture of isopropanol (IPA, 50 g) and water (25 g). Thiodiglycol was added (0.83 g) and the mixture stirred for 3 hr. at 50°C. Thioglycolic acid was then added (0.3 g) and stirring continued for 3 hours at 70°C.

The product (5% o.w.f.) was exhausted on to a scoured woollen fabric in the presence of Glaubers Salt (10% o.w.f.) at pH 4—5 (acetic acid), and a liquor ratio of 50:1. The temperature of the liquor was increased to 80°C by which time exhaustion was complete. The pH of the liquor was adjusted to 8—9 and the temperature held at 70°C for 10 min. The sample was removed from the bath, rinsed, hydro-extracted and dried at 100°C for 30 min. before wash testing for 3 hours as before. The results were as follows:

% Area Shrinkage

Treated	1%
Untreated	68%

Example X.

(Pyridinium and carboxyl groups)

Synthapret LKF was reacted with bromoacetic acid and the product dissolved in IPA/water as described in Example IX. Pyridine (0.54 g) was added and the mixture stirred for 3 hours at 50°C. Thioglycolic acid (0.31 g) was added and stirring continued for 3 hours at 70°C.

The product was exhausted on to woollen fabric, cured, dried and tested for shrinkage as in Example IX. The area shrinkage after 3 hours wash was 1%.

Example XI.

(Sulphonium and sulphonic acid groups)

Synthapret LKF was reacted with bromoacetic acid and the product dissolved in IPA/water as described in Example IX. Thiodiglycol (0.83 g) was added and the mixture heated at 70°C for 3 hours. Sodium sulphite (0.43 g) was added and the solution was heated at 70°C for 3 hours.

The product was exhausted on to woollen fabric, cured, dried and tested for shrinkage as in Example IX. The area shrinkage after 3 hours was zero.

Example XII.

(Pyridinium and sulphonic acid)

Synthappret LKF was reacted with bromoacetic acid and then with pyridine as described with Example IX. To the product was added sodium sulphite (0.43 g) dissolved in water (5 g). The solution was heated at 70°C for 3 hours.

The product was exhausted on to woollen fabric and cured as in Example IX and the treated fabric showed zero area shrinkage after washing for 3 hours as before.

Example XIII.

(Isothiuronium and carboxyl groups)

Synthappret LKF was reacted with bromoacetic acid and then dissolved in IPA/water as in Example IX. Thiourea (0.44 g) was added and the solution heated to 50°C for 3 hours. Thioglycolic acid (0.31 g) was added and heating continued for 5 hours at 70°C.

The product (5% o.w.f.) was exhausted on to woollen fabric at the boil and cured as in Example IX. The area shrinkage after wash testing for 3 hours was 0%.

Example XIV.

(Isothiuronium and sulphonic acid groups)

Synthappret LKF was reacted with bromoacetic acid followed by thiourea as in Example XIII. Sodium sulphite (0.43 g) dissolved in water (10 g) was added and the solution heated for 5 hours at 70°C.

The product (5% o.w.f.) was exhausted on to woollen fabric and cured and tested as in Example IX. The area shrinkage after testing was 0%.

Example XV.

(Azetidinium/carboxyl groups)

Synthappret LKF (11.5 g solids) was dissolved in ethyl acetate (20 g) and sulphuric acid (0.33 g) dissolved in ethyl acetate (5 g) added slowly with stirring. When the evolution of carbon dioxide had ceased, dried bromoacetic acid (0.48 g) was added.

Isopropanol (50 g), water (25 g) and epichlorohydrin (0.63 g) were added and the pH adjusted to 7-8 with sodium carbonate. The mixture was heated to 70°C for 15 min. Thioglycolic acid (0.31 g) was added and heating continued for 3 hours at 70°C.

The product was exhausted on to woollen fabric and cured and tested as described in Example IX. The area shrinkage after 3 hours washing was 2%.

Example XVI.

(Azetidinium/carbamoyl sulphonate)

Two-thirds of the isocyanate groups of Synthappret LKF (11.5 g) were hydrolysed by reaction with sulphuric acid as described in Example XV. The product was dissolved in isopropanol (50 g) and water (25 g) and a solution of sodium metabisulphite (0.6 g) in water (10 g) added. The pH of the solution was adjusted to 6 with sodium sulphite solution and it was stirred for 1 hour at room temperature. Epichlorohydrin (0.63 g) was added and the mixture heated to 60°C for 15 min.

The product (0.5 g solids) was dissolved in isopropanol (1 g) and then mixed with wetting agent (1.6 g of 10% Aerosol OT solution in IPA). This mixture was exhausted on to woollen fabric in the presence of 10% o.w.f. sodium sulphate at pH 4-5 and cured as described in Example IX. The area shrinkage after 3 hours washing was 2%.

Example XVII.

(Pyridinium/carbamoyl sulphonate)

Synthappret LKF (11.5 g) was partially reacted with dried bromoacetic acid (0.95 g) by heating for 4 hours at 70°C in ethyl acetate (10 g). The product was dissolved in isopropanol (50 g). To this was added a solution of sodium metabisulphite (0.5 g) in water (5 g). The pH was adjusted to a value of 6 by the addition of sodium sulphite. After 1 hour, pyridine (0.54 g) was added and the solution stirred for 4 hours at 40°C.

The product (5% o.w.f.) was exhausted on to a woollen fabric and cured as described in Example IX. The area shrinkage after 3 hours washing was 2%.

Example XVIII.

(Pyridinium/Bunte salt)

Synthappret LKF (11.5 solids) was reacted with dried bromoacetic acid (1.42 g) by heating for 4 hours at 70°C. To this was added isopropanol (50 g) and water (25 g). After adding pyridine (0.54 g) the solution was heated at 50°C for 2 hours. Sodium thiosulphate (0.54 g) was added and heating continued for 5 hours at 60°C.

The product (5% o.w.f.) was exhausted on to woollen fabric and cured as in Example IX. The area shrinkage after 3 hours washing was 3%.

Example XIX.

(Sulphonium and Bunte salt groups)

Synthappret LKF was reacted with bromoacetic acid, as described in Example IX. To the product, dissolved in isopropanol (50 g) and water (25 g) was added thiodiglycol (0.83 g). After heating at 50°C for 2 hours, sodium thiosulphate (0.54 g) was added. Heating was continued at 60°C for 2 hours.

The product was exhausted on to woollen fabric and cured as described in Example IX. The area shrinkage after 3 hours washing was 0%.

Example XX.

(Sulphonium and carbamoyl sulphonate)

Synthappret LKF (11.5 g) was reacted with bromoacetic acid (0.95 g) and the product dissolved in IPA/water, as described in Example XVII. To this solution was added a solution of sodium metabisulphite (0.5 g) in water (5 g). After 1 hour, thiodiglycol (0.83 g) was added and the temperature raised to 40°C for 45 min.

The product (5% o.w.f.) was exhausted on to a woollen fabric and cured as described in Example XVI. The area shrinkage was zero after 3 hours washing.

In the following Examples XXI to XXIII, other prepolymers are employed in the preparation of amphoteric polymers of this invention.

Helastic LV used in Example XXI is an aromatic analogue of Synthappret LKF being prepared by reaction of a similar polyether thiol with toluylene diisocyanate. In Examples XXII and XXIII the polymers are prepared from thiol-terminated prepolymers. Cationic protonated amino groups are introduced by the reaction of at least one of the thiol groups with a derivative of a diisocyanate in which one of the isocyanate groups has been hydrolysed with mineral acid.

Example XXI.

To Helastic LV (34 g), dissolved in ethyl acetate (20 g), was added very slowly, with stirring a solution of sulphuric acid (0.74 g) in ethyl acetate (10 g). After 30 mins. the product was dissolved in isopropanol (100 g) and water (20 g) and to this was added a solution of sodium bisulphite (3 g) in water (15 g) and triethylamine (0.5 g). Stirring was continued for 2 hours.

The product (5% o.w.f.) was exhausted on to a woollen fabric and cured as in Example XVI. The area shrinkage after 3 hours washing was 2%.

Example XXII.

To a solution of 2.5 g dicyclohexylmethane diisocyanate (Hylene W, Dupont) in ethyl acetate (50 g) was added, slowly with stirring, a solution of sulphuric acid (0.5 g) in ethyl acetate (10 g). The product was dissolved in toluene (25 g) together with a thiol terminated polyether triol derivative of molecular weight 3000—3500 (Oligan, Ciba-Geigy). Triethylamine (2 g) was added and the mixture heated to 60°C for 45 min.

The product (0.5 g solids), emulsified with an equal weight of an emulsifying agent (Lissapol NXX, ICI), was exhausted on to a single jersey fabric (10 g) in the presence of sodium sulphate (0.5 g) at pH 7—8 by raising the bath temperature to 80°C. After maintaining this temperature for 10 mins., alkali was added to bring the pH to a value of 9. The sample was removed after 10 min., hydroextracted and dried for 30 min. at 100°C, followed by 10 min. at 110°C. The area shrinkage after 1 hour machine washing (15 lb) was 2%.

Example XXIII.

A thiol-containing polymer was prepared by the following method.

A mixture of 100 grams (0.0995 mole) of a poly(tetramethylene oxide) diol of molecular weight approximately 1000 (Polymeg 1000), 19.9 grams (0.133 mole)

of 2-mercapto-succinic acid (thiomaleic acid), 50 ml of toluene and 2 g of toluene-4 sulphonie acid monohydrate was refluxed with stirring under nitrogen, with water of reaction and hydration being removed by azeotropic distillation in a Dean and Stark apparatus. After 1 hour, the predicted volume of water had accumulated in the receiver, and no more was observed to distil over during the next 30 minutes. The reaction mixture was cooled, further diluted with toluene, washed several times with water to remove the acid catalyst, and dried with anhydrous sodium sulphate. The solvent and other low molecular weight impurities were then removed under reduced pressure, yielding a colourless, viscous polymer.

The resulting carboxyl-terminated polymer containing on average four thiol groups per molecule was then used instead of the Oligan in the procedure of Example XXII and reacted with the partially acid-hydrolysed diisocyanate to give a product containing amine cationic groups and carboxyl anionic groups in the desired ratio as well as at least two residual cross-linkable thiol groups per molecule.

This product was soluble in alkaline solution and was exhausted from an aqueous bath at pH 7—8 and subsequently cured as described in Example XXII. An effective shrink-resist finish was achieved.

WHAT WE CLAIM IS:—

1. An amphoteric polymeric compound comprising at least one polymeric chain and both anionic and cationic groups and containing per molecule at least two groups capable of undergoing a cross-linking reaction either directly or by means of a cross-linking agent.

2. A polymeric compound according to Claim 1, wherein the anionic and/or cationic groups are themselves capable of undergoing a cross-linking reaction.

3. A polymeric compound according to Claim 1 or 2 wherein the polymeric chain is a polyether, polyamide, polyester or polyurethane.

4. A polymeric compound according to any of Claims 1 to 3 wherein the cationic groups are cross-linkable.

5. A polymeric compound according to any of Claims 1 to 4 wherein the cationic groups are protonated amino or azetidinium groups.

6. A polymeric compound according to any of Claims 1 to 4 wherein the cationic groups are sulphonium, isothiuronium or pyridinium groups.

7. A polymeric compound according to any of Claims 1 to 6 wherein the anionic groups are cross-linkable.

8. A polymeric compound according to Claim 7 wherein the anionic groups are thiosulphate or carbamoylsulphonate groups.

9. A polymeric compound according to any of Claims 1 to 6 wherein the anionic groups are carboxyl or sulphonie groups.

10. A polymeric compound according to any of Claims 1 to 3 wherein the cross-linkable groups are isocyanate groups.

11. A polymeric compound according to any of Claims 1 to 3 wherein the cross-linkable groups are thiol groups.

12. A polymeric compound according to Claim 2, 5 or 11 wherein the polymeric chain is a polyether and the anionic groups are carboxyl groups.

13. A method of preparing a polymeric compound according to Claim 1 which comprises reacting a prepolymer containing at least one polyether, polyester, polyamide or polyurethane chain and a plurality of reactive groups per molecule to introduce anionic and/or cationic and/or cross-linkable groups, as necessary, into the molecule and thereby form a polymeric compound containing cationic and anionic groups and at least two cross-linkable groups per molecule.

14. A method of preparing a polymeric compound according to Claim 5 in which the cationic groups are introduced by reacting an isocyanate-terminated prepolymer with mineral acid in organic solution.

15. A method according to Claim 14 wherein residual isocyanate groups in the reacted prepolymer are reacted with an alkali metal bisulphite.

16. A method of preparing a polymeric compound according to Claim 5 or 8 which comprises reacting a polyamide having pendant azetidinium and/or N-chlorohydrin groups with an alkali metal thiosulphate.

17. A method of preparing a polymeric compound according to Claim 6 in which the cationic groups are introduced by reacting an isocyanate-terminated prepolymer with a haloacetic acid and reacting the product with thiodiglycol, thiourea or pyridine.

18. A method of preparing a polymeric compound according to Claim 9 in which the anionic groups are introduced by reacting an isocyanate-terminated prepolymer with a haloacetic acid and reacting the product with thioglycollic acid.

19. A method of preparing a polymeric compound according to Claim 5 in which the cationic groups are introduced by at least partially hydrolysing an isocyanate-terminated prepolymer to form terminal amino groups and reacting the latter with epichlorohydrin and alkali to form azetidinium groups.
- 5 20. A method of preparing a polymeric compound according to Claim 12 which comprises reacting at least one thiol group of a prepolymer containing at least one polyether chain linked and/or terminated by thiol-containing dicarboxylic acid residues to introduce a cationic substituent group while forming a compound having at least two cross-linkable groups per molecule.
- 10 21. A process of treating keratinous fibres which comprises applying a polymeric compound according to any of Claims 1 to 12 by exhaustion from an aqueous bath and curing the polymeric compound on the fibres.
22. Wool having a shrink resist finish comprising the cured product of a polymeric compound according to any of Claims 1 to 12.

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